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<b>(21) International Application Number:</b> PCT/US99/18781 <b>(22) International Filing Date:</b> 18 August 1999 (18.08.99) <b>(30) Priority Data:</b> 09/141,168 27 August 1998 (27.08.98) US <b>(71) Applicant:</b> CHEVRON CHEMICAL COMPANY LLC [US/US]; 555 Market Street, San Francisco, CA 94105 (US). <b>(72) Inventors:</b> JERDEE, Gary, D.; 6402 Armitage, Orange, TX 77632 (US). LEONARD, James, P.; 545 Bret Harte Road, San Rafael, CA 94901 (US). CHING, Ta, Yen; 10 Santa Yorma Court, Novato, CA 94945 (US). GOODRICH, Joseph, L.; 3545 Wilkinson Lane, Lafayette, CA 94549 (US). RODGERS, Brad, D.; 3117 N. 23rd Street, Orange, TX 77630 (US). SCHMIDT, Richard, P.; 5212 Brookshire Estates Drive, Plainfield, IL 60544 (US). <b>(74) Agents:</b> GOODMAN, Kenneth, D. et al.; Williams, Morgan & Amerson, P.C., Suite 250, 7676 Hillmont, Houston, TX 77040 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> OXYGEN SCAVENGING PACKAGING  <b>(57) Abstract</b>  The present invention relates to a method of using oxygen scavenging material to a decrease oxidation and maintain product properties in packaged beverages, foods, oxygen sensitive materials or oxygen sensitive components comprising the steps of: a) incorporating an oxygen scavenging material into the structure of a container used to package beverages, foods, oxygen sensitive materials or oxygen sensitive components; b) placing beverages, foods, oxygen sensitive materials or oxygen sensitive components in the container; c) sealing the container; and d) storing the container at a temperature between 20 °F and 120 °F; wherein the oxygen scavenging material is selected from the group consisting of oxidizable polymers, ethylenically unsaturated polymers, benzylic polymers, allylic polymers, polybutadiene, poly[ethylene-methyl-acrylate-cyclohexene acrylate] terpolymers, poly[ethylene-vinylcyclohexene] copolymers, polylimonene resins, poly $\beta$ -pinene, poly $\alpha$ -pinene and a combination of a polymeric backbone, cyclic olefinic pendent groups and linking groups linking the olefinic pendent groups to the polymeric backbone.		

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1                                    **OXYGEN SCAVENGING PACKAGING**2                                    **CROSS-REFERENCE TO RELATED APPLICATIONS**

3    This application is a Continuation-in-Part of U.S. Application Serial  
4    No. 09/141,168, filed August 27, 1998.

5                                    **FIELD OF THE INVENTION**

6    The present invention relates to oxygen scavenging for use in packaging,  
7    such as in gable-top or rectangular cartons used to package food products,  
8    beverages, oxygen-sensitive materials and components.

9                                    **BACKGROUND OF THE INVENTION**

10   It is well known that regulating the exposure of oxygen-sensitive products to  
11   oxygen maintains and enhances the quality and "shelf-life" of the product. For  
12   instance, by limiting the exposure of oxygen sensitive food products to oxygen  
13   in a packaging system, the quality or freshness of food is maintained, spoilage  
14   reduced, and the food shelf life extended. In the food packaging industry,  
15   several means for regulating oxygen exposure have already been developed.  
16   These means include modified atmosphere packaging (MAP) and oxygen  
17   barrier film packaging.

18   For packaging material used in gable top or rectangular cartons, a coated  
19   paper or cardboard stock is often used. The coating for the paper or  
20   cardboard stock is usually a polymer-based resin, such as polyethylene,  
21   which can be applied to the paper or paperboard stock by extrusion coating or  
22   laminating. Such a coating serves not only to make the packaging material  
23   waterproof, but can also serve as an oxygen barrier.

24   In one known example of such an extrusion coated paper packaging material,  
25   the extrusion coating composition is comprised of greater than 20 and less

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1    than 98 weight percent of a high pressure low density polyethylene  
2    homopolymer and/or copolymer and greater than 2 and less than 80 weight  
3    percent of at least one linear low density ethylene hydrocarbon copolymer.

4    In an example of such a resin coated packaging material specifically designed  
5    to have enhanced oxygen barrier qualities, an additional layer of polyamide is  
6    added to the low density polyethylene laminated paperboard. In a similar  
7    example, an additional layer of heat-sealable ethylene vinyl alcohol copolymer  
8    is added to the low density polyethylene laminated paperboard.

9    One method currently being used for regulating oxygen exposure is "active  
10   packaging", whereby the package containing the food product has been  
11   modified in some manner to regulate the food's exposure to oxygen. One  
12   form of active packaging uses oxygen-scavenging sachets which contain a  
13   composition which scavenges the oxygen through oxidation reactions. One  
14   type of sachet contains iron-based compositions which oxidize to their ferric  
15   states. Another type of sachet contains unsaturated fatty acid salts on a  
16   particulate adsorbent. Yet another sachet contains metal/polyamide complex.  
17   However, one disadvantage of sachets is the need for additional packaging  
18   operations to add the sachet to each package. A further disadvantage arising  
19   from the iron-based sachets is that certain atmospheric conditions (e.g., high  
20   humidity, low CO<sub>2</sub> level) in the package are sometimes required in order for  
21   scavenging to occur at an adequate rate. Further, the sachets can present a  
22   problem to consumers if accidentally ingested.

23   Another means for regulating exposure of a packaged product to oxygen  
24   involves incorporating an oxygen scavenger into the packaging structure  
25   itself. A more uniform scavenging effect through the package is achieved by  
26   incorporating the scavenging material in the package instead of adding a  
27   separate scavenger structure (e.g., a sachet) to the package. This may be  
28   especially important where there is restricted airflow inside the package. In  
29   addition, incorporating the oxygen scavenger into the package structure

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1 provides a means of intercepting and scavenging oxygen as it permeates the  
2 walls of the package (herein referred to as an "active oxygen barrier"), thereby  
3 maintaining the lowest possible oxygen level in the package. Limited success  
4 has been achieved in incorporating oxygen scavenging material into the walls  
5 of packages for various types of food.

6 One attempt to prepare an oxygen-scavenging wall involves the incorporation  
7 of inorganic powders and/or salts. However, incorporation of these powders  
8 and/or salts causes reduction of the wall's optical transparency, discoloration  
9 after oxidation, and reduced mechanical properties such as tear strength. In  
10 addition, these compounds can lead to processing difficulties, especially when  
11 fabricating thin films. The oxidation products, which can be absorbed by food  
12 in the container, typically would not have FDA approval for human  
13 consumption.

14 Some oxygen scavenging systems produce an oxygen-scavenging wall. This  
15 is done by incorporating a metal catalyst-polyamide oxygen scavenging  
16 system into the package wall. Through catalyzed oxidation of the polyamide,  
17 the package wall regulates the amount of oxygen which reaches the interior  
18 volume of the package (active oxygen barrier) and has been reported to have  
19 oxygen scavenging rate capabilities up to about 5 cubic centimeters (cc)  
20 oxygen per square meter per day at ambient conditions. However, this  
21 system suffers from significant disadvantages.

22 One particularly limiting disadvantage of polyamide/catalyst materials can be  
23 a low oxygen scavenging rate. Adding these materials to a high-barrier  
24 package containing air can produce a package which is not generally suitable  
25 for creating the desired internal oxygen level.

26 There are also disadvantages to having the oxygen-scavenging groups in the  
27 backbone or network structure in this type of polyamide polymer. The basic  
28 polymer structure can be degraded and weakened upon reaction with oxygen.

1 This can adversely affect physical properties such as tensile or impact  
2 strength of the polymer. The degradation of the backbone or network of the  
3 polymer can further increase the permeability of the polymer to those  
4 materials sought to be excluded, such as oxygen.

5 Moreover, polyamides previously used in oxygen scavenging materials, such  
6 as MXD6, are typically incompatible with thermoplastic polymers used in most  
7 plastic packaging walls, such as ethylene-vinyl acetate copolymers and low  
8 density polyethylene. Even further, when such polyamides are used by  
9 themselves to make a package wall, they may result in inappropriately stiff  
10 structures. They also incur processing difficulties and higher costs when  
11 compared with the costs of thermoplastic polymers typically used to make  
12 flexible packaging. Even further, they are difficult to heat seal. Thus, all of  
13 these are factors to consider when selecting materials for packages,  
14 especially multi-layer flexible packages and when selecting systems for  
15 reducing oxygen exposure of packaged products.

16 Another approach to scavenging oxygen is an oxygen-scavenging  
17 composition comprising an ethylenically unsaturated hydrocarbon and a  
18 transition metal catalyst. Ethylenically unsaturated compounds such as  
19 squalene, dehydrated castor oil, and 1,2-polybutadiene are useful oxygen  
20 scavenging compositions, and ethylenically saturated compounds such as  
21 polyethylene and ethylene copolymers are useful as diluents. Compositions  
22 utilizing squalene, castor oil, or other such unsaturated hydrocarbon typically  
23 have an oily texture as the compound migrates toward the surface of the  
24 material. Further, polymer chains which are ethylenically unsaturated in the  
25 backbone would be expected to degrade upon scavenging oxygen,  
26 weakening the polymer due to polymer backbone breakage, and generating a  
27 variety of off-odor, off-taste by-products.

28 Oxygen scavenging layers extruded or laminated onto the surface of  
29 paperboard stock have been tried with limited success. In one of these

1 examples, the oxygen scavenging layer is an ethylenically unsaturated  
2 hydrocarbon and a transition metal catalyst. Other known examples of an  
3 oxygen scavenging layer that can be coated onto the surface of paper board  
4 stock and which furthermore retain oxygen scavenging capabilities at low  
5 temperatures are atactic-1,2-polybutadiene, EPDM rubbers, polyoctenamer,  
6 and 1,4-polybutadiene.

7 An oxygen-scavenging composition comprising a blend of a first polymeric  
8 component comprising a polyolefin is known, the first polymeric component  
9 having been grafted with an unsaturated carboxylic anhydride or an  
10 unsaturated carboxylic acid, or combinations thereof, or with an epoxide; a  
11 second polymeric component having -OH, -SH, or -NHR<sup>2</sup> groups where R<sup>2</sup> is  
12 H, C<sub>1</sub>-C<sub>3</sub> alkyl, substituted C<sub>1</sub>-C<sub>3</sub> alkyl; and a catalytic amount of metal salt  
13 capable of catalyzing the reaction between oxygen and the second polymeric  
14 component, the polyolefin being present in an amount sufficient so that the  
15 blend is non phase-separated. A blend of polymers is utilized to obtain  
16 oxygen scavenging, and the second polymeric component is preferably a  
17 polyamide or a copolyamide such as the copolymer of m-xylylene-diamine  
18 and adipic acid (MXD6).

19 Other oxidizable polymers recognized in the art include "highly active"  
20 oxidizable polymers such as poly(ethylene-methyl acrylate-benzyl acrylate),  
21 EBZA, and poly(ethylene-methyl acrylate-tetrahydrofuryl acrylate), EMTF, as  
22 well as poly(ethylene-methyl acrylate-nopol acrylate), EMNP. Blends of  
23 suitable polymers are also acceptable, such as a blend of EMTF and  
24 poly-d-limonene. Although effective as oxygen scavengers, these polymers  
25 have the drawback of giving off a strong odor before oxygen scavenging and  
26 large amounts of volatile byproducts before and after oxygen scavenging.

27 Also known are oxygen-scavenging compositions which comprise a transition-  
28 metal salt and a compound having an ethylenic or polyethylenic backbone  
29 and having allylic pendent or terminal moieties which contain a carbon atom

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1 that can form a free radical that is resonance-stabilized by an adjacent group.  
2 Such a polymer needs to contain a sufficient amount and type of transition  
3 metal salt to promote oxygen scavenging by the polymer when the polymer is  
4 exposed to an oxygen-containing fluid such as air. Although effective as  
5 oxygen scavengers, upon oxidation, it has been found that allylic pendent  
6 groups on an ethylenic or polyethylenic backbone tend to generate  
7 considerable amounts of organic fragments. It is believed that this is a result  
8 of oxidative cleavage. These fragments can interfere with the use of allylic  
9 pendent groups as oxygen scavengers in food packaging by generating  
10 compounds that can affect taste and odor of the packaged products.

11 The present invention solves many of the problems of the prior art  
12 encountered when oxygen scavenging material has been incorporated into  
13 packaging materials. In various specific embodiments, the present invention  
14 solves many of the particular problems encountered with incorporating oxygen  
15 scavenging material into the structure of food packaging material such as  
16 paperboard stock for gable-top or rectangular cartons.

#### 17 SUMMARY OF THE INVENTION

18 In one embodiment, the present invention relates to a method of using oxygen  
19 scavenging material to decrease oxidation and maintain product properties in  
20 packaged beverages, foods, oxygen sensitive materials or oxygen sensitive  
21 components comprising the steps of:

22 (a) incorporating an oxygen scavenging material into the structure of a  
23 container used to package beverages, foods, oxygen sensitive materials  
24 or oxygen sensitive components;

25 (b) placing beverages, foods, oxygen sensitive materials or oxygen  
26 sensitive components in the container;



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1 (c) sealing the container; and

2 (d) storing the container at a temperature between 20°F and 120°F;

3 wherein the oxygen scavenging material is selected from the group consisting  
4 of oxidizable polymers, ethylenically unsaturated polymers, benzylic polymers,  
5 allylic polymers, polybutadiene, poly[ethylene-methyl acrylate-cyclohexene  
6 acrylate] terpolymers, poly[ethylene-vinylcyclohexene] copolymers,  
7 polylimonene resins, poly  $\beta$ -pinene, poly  $\alpha$ -pinene and a combination of a  
8 polymeric backbone, cyclic olefinic pendent groups and linking groups linking  
9 the olefinic pendent groups to the polymeric backbone.

10 The foregoing embodiment is particularly applicable to gable top or  
11 rectangular cartons particularly when they contain a juice such as orange  
12 juice. It has been found that the most preferred oxygen scavenging material  
13 is a combination of a polymeric backbone, cyclic olefinic pendent groups and  
14 linking groups linking the olefinic pendent groups to the polymeric backbone.

15 In another embodiment, the invention relates to a method of storing  
16 beverages, foods, oxygen-sensitive materials or oxygen-sensitive  
17 components for an extended period while maintaining product properties  
18 comprising the steps of:

19 (a) incorporating an oxygen scavenging material into the structure of a  
20 container used to package beverages, foods, oxygen-sensitive materials  
21 or oxygen-sensitive components;

22 (b) placing beverages, foods, oxygen sensitive materials or oxygen  
23 sensitive components in the container;

24 (c) sealing the container; and

1 (d) storing the container at a temperature between 20°F and 120°F;

2 wherein the oxygen scavenging material is selected from the group consisting  
3 of oxidizable polymers, ethylenically unsaturated polymers, benzylic polymers,  
4 allylic polymers, polybutadiene, poly[ethylene-methyl acrylate-cyclohexene  
5 acrylate] terpolymers, poly[ethylene-vinylcyclohexene] copolymers,  
6 polylimonene resins, poly  $\beta$ -pinene, poly  $\alpha$ -pinene and a combination of a  
7 polymeric backbone, cyclic olefinic pendent groups and linking groups linking  
8 the olefinic pendent groups to the polymeric backbone.

9 The foregoing embodiment is particularly applicable to gable top or  
10 rectangular cartons particularly when they contain a juice such as orange  
11 juice. It has been found that the most preferred oxygen scavenging material  
12 is a combination of a polymeric backbone, cyclic olefinic pendent groups and  
13 linking groups linking the olefinic pendent groups to the polymeric backbone.

14 In yet another embodiment, the present invention relates to a rigid paperboard  
15 container, the container being constructed from extrusion coated or laminated  
16 paperboard comprising:

17 (a) a paperboard substrate having opposed inner and outer surfaces;

18 (b) a first polymer layer coated or laminated onto the outer surface of said  
19 paperboard substrate; and

20 (c) an inner, product contact sandwich layer comprising an oxygen barrier  
21 layer and an oxygen scavenging layer;

22 wherein the oxygen scavenging material is selected from the group consisting  
23 of oxidizable polymers, ethylenically unsaturated polymers, benzylic polymers,  
24 allylic polymers, polybutadiene, poly[ethylene-methyl acrylate-cyclohexene  
25 acrylate] terpolymers, poly[ethylene-vinylcyclohexene] copolymers,

- 1 polylimonene resins, poly  $\beta$ -pinene, poly  $\alpha$ -pinene and a combination of a  
2 polymeric backbone, cyclic olefinic pendent groups and linking groups linking  
3 the olefinic pendent groups to the polymeric backbone.
- 4 The foregoing embodiment is particularly applicable to gable top or  
5 rectangular cartons particularly when they contain a juice such as orange  
6 juice. It has been found that the most preferred oxygen scavenging material  
7 to use is a combination of a polymeric backbone, cyclic olefinic pendent  
8 groups and linking groups linking the olefinic pendent groups to the polymeric  
9 backbone.

10 DESCRIPTION OF THE DRAWINGS

- 11 Figure 1 is a graph showing the measured vitamin C retention in orange juice  
12 packaged in glass container, PBL and OS cartons as described in Example 1.  
13 The graph is plotted as mg/liter vitamin C vs. time.
- 14 Figure 2 is a graph showing the measured dissolved oxygen in orange juice  
15 packaged in glass container, PBL and OS cartons as described in Example 1.  
16 The graph is plotted as mg/liter oxygen vs. time.
- 17 Figure 3 is a graph showing the measured vitamin C retention in orange juice  
18 packaged in OS and PBL cartons with OS films as described in Example 1.  
19 The graph is plotted as mg/liter vitamin C vs. time.
- 20 Figure 4 is a graph showing the measured dissolved oxygen in OS and PBL  
21 cartons with OS films as described in Example 1. The graph is plotted as  
22 mg/liter oxygen vs. time.

1                    DETAILED DESCRIPTION OF THE INVENTION

2    The oxygen scavenging system of the present invention has a number of  
3    benefits including, but not limited to: extending shelf life; preserving product  
4    color; improving taste and odor; reducing mold growth; and retaining vitamin  
5    and other nutritional value.

6    Because these scavengers are actually part of the package, they eliminate  
7    the additional handling steps and safety concerns associated with oxygen  
8    scavenging sachets. In fact, the oxygen scavenging system of the present  
9    invention could be incorporated into an existing packaging structure without  
10   any consumer awareness of change in the package appearance.

11   The oxygen scavenging polymers can be incorporated into a layer of a film or  
12   rigid package using standard extrusion equipment. Because the scavenger  
13   material permeates an entire layer incorporated into the package wall, the  
14   capacity per cost of scavenger compares very favorably to systems where the  
15   scavenger is added into the package wall in some fashion.

16   This invention relates to the use of oxygen scavengers in packaging  
17   materials, for example, extrusion-coated, rigid containers. In a more specific  
18   embodiment, the containers are in the form of gable top and rectangular  
19   cartons, for beverages, foods, and other oxygen sensitive materials and  
20   components. A non-limiting list of possible products include fruit juices,  
21   prepared foods, snack foods, as well as other oxygen-sensitive materials such  
22   as chemicals and oxygen-sensitive components, such as computer parts.

23   The containers in the present invention can be filled under either aseptic  
24   packaging conditions or under cold-filled packaging conditions, without the  
25   specific procedures used for aseptic packaging conditions (which is how the  
26   samples discussed in the Examples are prepared).

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1 A non-limiting description of a typical procedure used for aseptic packaging  
2 conditions for carton containers is as follows. The packaging materials are  
3 formed into cartons and sterilized in the filler machine with hot hydrogen  
4 peroxide vapor. Once the vapor is evaporated with hot, sterile air or  
5 ultraviolet light, the sterilized package is filled at ambient temperature with the  
6 sterilized product and then sealed within a sterile zone.

7 By incorporating an oxygen scavenging layer as an inner layer in the walls of  
8 the packaging material or as a strip attached somewhere on the inner surface  
9 of the packaging material, oxidation of product properties, such as the  
10 nutritional value in beverages or foods, is reduced significantly.

11 In a preferred embodiment, the oxygen scavengers are combined with a  
12 transition-metal salt to catalyze the oxygen scavenging properties of the  
13 materials. A transition-metal salt, as the term is used here, comprises an  
14 element chosen from the first, second and third transition series of the  
15 periodic table of the elements, particularly one that is capable of promoting  
16 oxygen scavenging. This transition-metal salt is in a form, which facilitates or  
17 imparts scavenging of oxygen by the composition of this invention. A  
18 plausible mechanism, not intended to place limitations on this invention, is  
19 that the transition element can readily inter-convert between at least two  
20 oxidation states and facilitates formation of free radicals. Suitable transition-  
21 metal elements include, but are not limited to, manganese II or III, iron II or III,  
22 cobalt II or III, nickel II or III, copper I or II, rhodium II, III or IV, and ruthenium.  
23 The oxidation state of the transition-metal element when introduced into the  
24 composition is not necessarily that of the active form. It is only necessary to  
25 have the transition-metal element in its active form at or shortly before the  
26 time that the composition is required to scavenge oxygen. The transition-  
27 metal element is preferably iron, nickel or copper, more preferably  
28 manganese, and most preferably cobalt.

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1    Suitable counter-ions for the transition metal element are organic or inorganic  
2    anions. These include, but are not limited to, chloride, acetate, stearate,  
3    oleate, palmitate, 2-ethylhexanoate, citrate, glycolate, benzoate,  
4    neodecanoate or naphthenate. Organic anions are preferred. Particularly  
5    preferable salts include cobalt 2-ethylhexanoate, cobalt benzoate, cobalt  
6    stearate, cobalt oleate and cobalt neodecanoate. The transition-metal  
7    element may also be introduced as an ionomer, in which case a polymeric  
8    counter-ion is employed.

9    The composition of the present invention when used in forming an oxygen  
10    scavenging packaging article can be composed solely of the above-described  
11    polymer and transition metal catalyst. However, components, such as  
12    photoinitiators, can be added to further facilitate and control the initiation of  
13    oxygen scavenging properties. For instance, it is often preferable to add a  
14    photoinitiator, or a blend of different photoinitiators, to the oxygen scavenger  
15    compositions, especially when antioxidants are included to prevent premature  
16    oxidation of that composition during processing.

17    Suitable photoinitiators are well known in the art. Such photoinitiators are  
18    discussed in U.S. Patent Application Serial No. 08/857,325 in which some of  
19    the present inventors were contributing inventors and which is incorporated  
20    herein by reference. Specific examples include, but are not limited to,  
21    benzophenone, o-methoxy-benzophenone, acetophenone, o-methoxy-  
22    acetophenone, acenaphthenequinone, methyl ethyl ketone, valerophenone,  
23    hexanophenone,  $\alpha$ -phenyl-butyrophenone, p-morpholinopropiophenone,  
24    dibenzosuberone, 4-morpholinobenzophenone, benzoin, benzoin methyl  
25    ether, 4-o-morpholinodeoxybenzoin, p-diacetylbenzene,  
26    4-aminobenzophenone, 4'-methoxyacetophenone, substituted and  
27    unsubstituted anthraquinones,  $\alpha$ -tetralone, 9-acetylphenanthrene, 2-acetyl-  
28    phenanthrene, 10-thioxanthenone, 3-acetyl-phenanthrene, 3-acetylindole,  
29    9-fluorenone, 1-indanone, 1,3,5-triacetylbenzene, thioxanthen-9-one,  
30    xanthene-9-one, 7-H-benz[de]anthracen-7-one, benzoin tetrahydropyranyl

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1 ether, 4,4'-bis(dimethylamino)-benzophenone, 1'-acetonaphthone,  
2 2'-acetonaphthone, acetophenone and 2,3-butanedione,  
3 benz[a]anthracene-7,12-dione, 2,2-dimethoxy-2-phenylacetophenone,  
4  $\alpha,\alpha$ -diethoxy-acetophenone,  $\alpha,\alpha$ -dibutoxyacetophenone, etc. Singlet oxygen  
5 generating photosensitizers such as Rose Bengal, methylene blue, and  
6 tetraphenyl porphine may also be employed as photoinitiators. Polymeric  
7 initiators include polyethylene carbon monoxide and oligo[2-hydroxy-2-methyl-  
8 1-[4-(1-methylvinyl)phenyl]propanone]. Use of a photoinitiator is preferable  
9 because it generally provides faster and more efficient initiation. When actinic  
10 radiation is used, the initiators may also provide initiation at longer  
11 wavelengths which are less costly to generate and less harmful.

12 When a photoinitiator is used, its primary function is to enhance and facilitate  
13 the initiation of oxygen scavenging upon exposure to radiation. The amount  
14 of photoinitiator can vary. In many instances, the amount will depend on the  
15 amount and type of monomers present in the present invention, the  
16 wavelength and intensity of radiation used, the nature and amount of  
17 antioxidants used, as well as the type of photoinitiator used. The amount of  
18 photoinitiator also depends on how the scavenging composition is used. For  
19 instance, if the photoinitiator-coating composition is placed underneath a  
20 layer, which is somewhat opaque to the radiation used, more initiator may be  
21 needed. For most purposes, however, the amount of photoinitiator, when  
22 used, will be in the range of 0.01 to 10% by weight of the total composition.  
23 The initiating of oxygen scavenging can be accomplished by exposing the  
24 packaging article to actinic or electron beam radiation, as described below.

25 Antioxidants may be incorporated into the scavenging compositions used in  
26 this invention to control degradation of the components during compounding  
27 and shaping. An antioxidant, as defined herein, is any material, which inhibits  
28 oxidative degradation or cross-linking of polymers. Typically, such  
29 antioxidants are added to facilitate the processing of polymeric materials  
30 and/or prolong their useful lifetime.

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1 Antioxidants such as Vitamin E, Irganox® 1010, 2,6-di(t-butyl)-4-methyl-  
2 phenol(BHT), 2,2'-methylene-bis(6-t-butyl-p-cresol), triphenylphosphite,  
3 tris-(nonylphenyl)phosphite and dilaurylthiodipropionate would be suitable for  
4 use with this invention.

5 When an antioxidant is included as part of the packaging, it should be used in  
6 amounts which will prevent oxidation of the scavenger composition's  
7 components as well as other materials present in a resultant blend during  
8 formation and processing but the amount should be less than that which  
9 would interfere with the scavenging activity of the resultant layer, film or article  
10 after initiation has occurred. The particular amount needed will depend on the  
11 particular components of the composition, the particular antioxidant used, the  
12 degree and amount of thermal processing used to form the shaped article,  
13 and the dosage and wavelength of radiation applied to initiate oxygen  
14 scavenging and can be determined by conventional means. Typically, they  
15 are present in about 0.01 to 1% by weight.

16 Other additives which may also be included in oxygen scavenger layers  
17 include, but are not necessarily limited to, fillers, pigments, dyestuffs,  
18 stabilizers, processing aids, plasticizers, fire retardants, anti-fog agents, etc.

19 The amounts of the components which are used in the oxygen scavenging  
20 compositions, or layers have an effect on the use, effectiveness and results of  
21 this method. Thus, the amounts of polymer, transition metal catalyst and any  
22 photoinitiator, antioxidant, polymeric diluents and additives, can vary  
23 depending on the article and its end use.

24 For instance, one of the primary functions of the polymer described above is  
25 to react irreversibly with oxygen during the scavenging process, while the  
26 primary function of the transition metal catalyst is to facilitate this process.  
27 Thus, to a large extent, the amount of polymer present will affect the oxygen  
28 scavenging capacity of the composition, i.e., affect the amount of oxygen that



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1 the composition can consume. The amount of transition metal catalyst will  
2 affect the rate at which oxygen is consumed. Because it primarily affects the  
3 scavenging rate, the amount of transition metal catalyst may also affect the  
4 induction period.

5 Any further additives employed normally will not comprise more than 10% of  
6 the scavenging composition, with preferable amounts being less than 5% by  
7 weight of the scavenging composition.

8 Optionally, the methods of this invention can include exposure of the polymer  
9 containing the oxygen scavenging-promoting transition metal catalyst to  
10 actinic radiation to reduce the induction period, if any, before oxygen  
11 scavenging commences. A method is known for initiating oxygen scavenging  
12 by exposing a film comprising an oxidizable organic compound and a  
13 transition metal catalyst to actinic radiation. Such methods are discussed in  
14 U.S. Patent No. 5,211,875, the disclosure of which patent is incorporated  
15 herein by reference. A composition of the present invention which has a long  
16 induction period in the absence of actinic radiation but a short or non-existent  
17 induction period after exposure to actinic radiation is particularly preferred.  
18 Compositions which are activated by actinic radiation can be stored without  
19 special preparation or storage requirements, such as being packaged or kept  
20 in a nitrogen environment. They maintain a high capability for scavenging  
21 oxygen upon activation with actinic radiation. Thus, oxygen scavenging can  
22 be activated when desired.

23 The radiation used in this method could be light, e.g., ultraviolet or visible light  
24 having a wavelength of about 200 to 750 nanometers (nm), and preferably  
25 having a wavelength of about 200 to 600 nm, and most preferably from about  
26 200 to 400 nm. When employing this method, it is preferable to expose the  
27 oxygen scavenger to at least 1 Joule per gram of scavenging composition. A  
28 typical amount of exposure is in the range of 10 to 2000 Joules per gram.  
29 The radiation can also be an electron beam radiation at a dosage of about 2

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1 to 200 kiloGray, preferably about 10 to 100 kiloGray. Other sources of  
2 radiation include ionizing radiation such as gamma, X-rays and corona  
3 discharge. The duration of exposure depends on several factors including,  
4 but not limited to, the amount and type of photoinitiator present, thickness of  
5 the layers to be exposed, thickness and opacity of intervening layers, amount  
6 of any antioxidant present, and the wavelength and intensity of the radiation  
7 source. The radiation provided by heating of polyolefin and the like polymers  
8 (e.g., 100-250°C) during processing does not enable triggering to take effect.

9 In various specific embodiments, the use of oxygen-scavenging compositions  
10 in the present invention can be accomplished by coating oxygen scavenging  
11 composition onto materials such as metallic foil, polymer film, metallized film,  
12 paper or cardboard to provide oxygen scavenging properties. The  
13 compositions are also useful in making articles such as single or multi-layer  
14 rigid thick-walled plastic containers or bottles (typically, between 8 and  
15 100 mils in thickness) or in making single or multi-layer flexible films,  
16 especially thin films (less than 3 mil, or even as thin as about 0.25 mil). Some  
17 of the compositions of the present invention are easily formed into films using  
18 well-known means. These films can be used alone or in combination with  
19 other films or materials.

20 The compositions used in the present invention may be further combined with  
21 one or more polymers, such as thermoplastic polymers which are typically  
22 used to form film layers in plastic packaging articles. In the manufacture of  
23 certain packaging articles, well-known thermosets can also be used as a  
24 polymeric diluent.

25 Selecting combinations of a diluent and the composition used in the present  
26 invention depends on the properties desired. Polymers which can be used as  
27 the diluent include, but are not limited to, polyethylene, low or very low density  
28 polyethylene, polypropylene, polyvinyl chloride, and ethylene copolymers  
29 such as ethylene-vinyl acetate, ethylene-alkyl acrylates or methacrylates,

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1 ethylene-acrylic acid or methacrylic acid, and ethylene-arylic or methacrylic  
2 acid ionomers. In rigid packaging applications, polystyrene is used; and in  
3 rigid articles such as beverage containers, polyethylene terephthalate (PET) is  
4 often used. Blends of different diluents may also be used. However, as  
5 indicated above, the selection of the polymeric diluent largely depends on the  
6 article to be manufactured and the end use. Such selection factors are well  
7 known in the art.

8 If a diluent polymer such as a thermoplastic is employed, it should further be  
9 selected according to its compatibility with the composition of the present  
10 invention. In some instances, the clarity, cleanliness, effectiveness as an  
11 oxygen-scavenger, barrier properties, mechanical properties and/or texture of  
12 the article can be adversely affected by a blend containing a polymer which is  
13 incompatible with the composition of the present invention.

14 A blend of a composition used in the present invention with a compatible  
15 polymer can be made by dry blending or by melt-blending the polymers  
16 together at a temperature in the approximate range of 50°C to 250°C.  
17 Alternative methods of blending include the use of a solvent followed by  
18 evaporation. When making film layers or articles from oxygen-scavenging  
19 compositions, extrusion or coextrusion, solvent casting, injection molding,  
20 stretch blow molding, orientation, thermoforming, extrusion coating, coating  
21 and curing, lamination or combinations thereof would typically follow the  
22 blending.

23 Layers in the package wall of the present invention may be in several forms.  
24 They may be in the form of stock films, including "oriented" or "heat  
25 shrinkable" films, which may ultimately be processed as bags, etc., or in the  
26 form of stretch-wrap films. The layers may also be in the form of sheet inserts  
27 to be placed in a packaging cavity. In a preferred embodiment of a rigid  
28 paperboard beverage container, the layer may be within the container's walls.  
29 Even further, the layer may also be in the form of a liner placed with or in the

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1 container's lid or cap. The layer may even be coated or laminated onto any  
2 one of the articles mentioned above.

3 In multi-layered articles, the scavenging layer used in the present invention  
4 may be included with layers such as, but not necessarily limited to, "oxygen  
5 barriers", i.e., a layer of material having an oxygen transmission rate equal to  
6 or less than 500 cubic centimeters per square meter ( $\text{cc/m}^2$ ) per day per  
7 atmosphere at room temperature, i.e. about 25°C. Typical oxygen barriers  
8 are poly(ethylene vinyl alcohol) ("EVOH"), polyacrylonitrile, polyvinyl chloride,  
9 poly(vinylidene dichloride), polyethylene terephthalate, silica, and polyamides.  
10 Metal foil layers can also be employed.

11 The polyvinylchloride ("PVC") and poly(vinylidene dichloride) ("PVDC")  
12 materials include normally crystalline polymers, both homopolymers and  
13 copolymers, containing vinylidene chloride. Copolymerizable materials such  
14 as vinyl chloride, acrylonitrile, vinyl acetate, ethyl acrylate, ethyl methacrylate  
15 and methyl methacrylate can be used. Terpolymers can also be employed,  
16 e.g., a terpolymer of vinylidene chloride, dimethyl maleate and vinyl chloride.

17 The term "polyamide" refers to high molecular weight polymers having amide  
18 linkages along the molecular chain, and refers more specifically to synthetic  
19 polyamide such as various Nylons such as Nylon 6, 66, 6/12, 6/66 and 6/69,  
20 including high density versions and nylon copolymers.

21 To determine the oxygen scavenging capabilities of a composition, the rate of  
22 oxygen scavenging can be calculated by measuring the time that elapsed  
23 before the article depletes a certain amount of oxygen from a sealed  
24 container. For instance, a film comprising the scavenging component can be  
25 placed in an air-tight, sealed container of a certain oxygen containing  
26 atmosphere, e.g., air which typically contains 20.9% oxygen by volume.  
27 Then, over a period of time, samples of the atmosphere inside the container  
28 are removed to determine the percentage of oxygen remaining. The

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1 scavenging rates of the compositions and layers used in the present invention  
2 will change with changing temperature and atmospheric conditions.

3 When an active oxygen barrier is prepared, the scavenging rate can be as low  
4 as 0.1 cc oxygen per gram of composition of the present invention per day in  
5 air at 25°C and 1 atmosphere pressure. However, preferable compositions of  
6 this invention have rates equal to or greater than 1 cc oxygen per gram per  
7 day, thus making them suitable for scavenging oxygen from within a package,  
8 as well as suitable for active oxygen barrier applications. Many compositions  
9 are even capable of more preferable rates equal to or greater than 5.0 cc O<sub>2</sub>  
10 per gram per day.

11 In an active oxygen barrier application, it is preferable that the combination of  
12 oxygen barriers and any oxygen scavenging activity create an overall oxygen  
13 transmission rate of less than about 1.0 cubic centimeter-mil per square meter  
14 per day per atmosphere pressure at 25°C. Another definition of acceptable  
15 oxygen scavenging is derived from testing actual packages. In actual use, the  
16 scavenging rate requirement will largely depend on the internal atmosphere of  
17 the package, the contents of the package and the temperature at which it is  
18 stored.

19 In a packaging article made according to this invention, the scavenging rate  
20 will depend primarily on the amount and nature of the composition of the  
21 present invention in the article, and secondarily on the amount and nature of  
22 other additives (e.g., diluent polymer, antioxidant, etc.) which are present in  
23 the scavenging component, as well as the overall manner in which the  
24 package is fabricated, e.g., surface area/volume ratio.

25 The oxygen scavenging capacity of an article comprising the invention can be  
26 measured by determining the amount of oxygen consumed until the article  
27 becomes ineffective as a scavenger. The scavenging capacity of the package

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1 will depend primarily on the amount and nature of the scavenging moieties  
2 present in the article, as discussed above.

3 In actual use, the oxygen scavenging capacity requirement of the article  
4 largely depends on three parameters of each application:

5 (1) the quantity of oxygen initially present in the package;

6 (2) the rate of oxygen entry into the package in the absence of the  
7 scavenging property; and

8 (3) the intended shelf life for the package.

9 The scavenging capacity of the composition can be as low as 1 cc oxygen per  
10 gram, but is preferably at least 10 cc oxygen per gram, and more preferably at  
11 least 50 cc oxygen per gram. When such compositions are in a layer, the  
12 layer will preferably have an oxygen capacity of at least 250 cc oxygen per  
13 square meter per mil thickness and more preferably at least 500 cc oxygen  
14 per square meter per mil thickness.

15 In a preferred embodiment, the present invention relates to a rigid paperboard  
16 container which is constructed from extrusion coated or laminated  
17 paperboard. The paperboard container comprises a paperboard substrate  
18 with opposed inner and outer surfaces, the inner surface being the side of the  
19 paperboard substrate which has contact with the air inside the container and  
20 the outer surface being the side of the paperboard substrate which has  
21 contact with the air outside the container.

22 The outer surface of the paperboard substrate is coated or laminated with at  
23 least one polymer layer and the inner surface of the paperboard substrate is  
24 coated with at least an oxygen barrier layer and an oxygen scavenging layer.  
25 The polymer layer can be low density polyethylene polymer, linear low density

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1 polyethylene polymer, a blend of low density polyethylene polymer and linear  
2 low density polyethylene polymer, or a coextrusion of low density polyethylene  
3 polymer and linear low density polyethylene polymer. The oxygen barrier  
4 layer can be, among other things, metallized film, such as foil, ethylene vinyl  
5 alcohol (EVOH) or polyamides.

6 In one embodiment of the inner surface of the above-described invention,  
7 there is at least one adhesive tie layer adjacent to the oxygen barrier layer.  
8 Adhesive tie layers may be made of various polymeric adhesives, especially  
9 anhydride grafted polymers, copolymers or terpolymers as well as maleic  
10 anhydride and rubber modified polymers. In another embodiment of the  
11 above-described embodiment of the invention, an adhesive tie layer is  
12 juxtaposed between the barrier layer and the polymer layer coated or  
13 laminated onto the inner surface of the paperboard substrate. In a more  
14 preferred embodiment of the tie layer, the materials used are ionomers,  
15 specifically zinc ionomers or sodium ionomers. In another more preferred  
16 embodiment of the above-described embodiments of the invention, the tie  
17 layer of the inner, product contact, sandwich layer comprises ethylene acrylic  
18 acid. In another more preferred embodiment, the tie layer of the inner product  
19 contact sandwich layer comprises ethylene methacrylic acid.

20 In another preferred embodiment of the above-described embodiment of the  
21 invention, the inner product contact sandwich layer further comprises a  
22 polymer layer coating or laminating the innermost surface of the inner product  
23 contact sandwich layer. The polymer layer can be low density polyethylene  
24 polymer, linear low density polyethylene polymer, a blend of low density  
25 polyethylene polymer and linear low density polyethylene polymer, or a  
26 coextrusion of low density polyethylene polymer and linear low density  
27 polyethylene polymer.

28 In another preferred embodiment of the above-described embodiment of the  
29 invention, a second polymer layer is coated or laminated onto the inner

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1 surface of the paperboard substrate. This second polymer layer can be low  
2 density polyethylene polymer, linear low density polyethylene polymer, a  
3 blend of low density polyethylene polymer and linear low density polyethylene  
4 polymer, and a coextrusion of low density polyethylene polymer and linear low  
5 density polyethylene polymer.

6 In yet another preferred embodiment of the above-described embodiment of  
7 the invention, a third polymer layer is coated or laminated onto the inner  
8 surface of the oxygen scavenging layer of the inner, product contact,  
9 sandwich layer. This third polymer layer can be low density polyethylene  
10 polymer, linear low density polyethylene polymer, a blend of low density  
11 polyethylene polymer and linear low density polyethylene polymer, and a  
12 coextrusion of low density polyethylene polymer and linear low density  
13 polyethylene polymer.

14 In still another preferred embodiment of the above-described embodiment of  
15 the invention, the inner product contact sandwich layer further comprises a  
16 fourth polymer layer and a second oxygen scavenging layer, the second  
17 oxygen scavenging layer being on the inner surface of the third polymer layer  
18 and the fourth polymer layer coating or laminating the inner surface of the  
19 second oxygen scavenging layer. This second polymer layer can be low  
20 density polyethylene polymer, linear low density polyethylene polymer, a  
21 blend of low density polyethylene polymer and linear low density polyethylene  
22 polymer, and a coextrusion of low density polyethylene polymer and linear low  
23 density polyethylene polymer.

24 In yet another preferred embodiment of the above-described embodiment of  
25 the invention, a tie layer is coated or laminated onto the inner surface of the  
26 oxygen scavenging layer and an ethylene vinyl alcohol layer is coated or  
27 laminated onto the inner surface of the tie layer coating or laminating the inner  
28 surface of the oxygen scavenging layer.



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1 In still another preferred embodiment of the above-described embodiment of  
2 the invention, the inner product contact sandwich layer further comprises a  
3 second barrier layer and a second tie layer, the second barrier layer being on  
4 the inner surface of the first tie layer and the second tie layer being  
5 juxtaposed between the inner surface of the second barrier layer and the  
6 outer surface of the oxygen scavenging layer.

7 In a more preferred embodiment of the above-described embodiments of the  
8 invention, the oxygen scavenging material is selected from the group  
9 consisting of oxidizable polymers, ethylenically unsaturated polymers,  
10 benzylic polymers, allylic polymers, polybutadiene, poly[ethylene-methyl  
11 acrylate-cyclohexene acrylate] terpolymers, poly[ethylene-vinylcyclohexene]  
12 copolymers, polylimonene resins, poly  $\beta$ -pinene and poly  $\alpha$ -pinene.

13 In a more preferred embodiment of the above-described embodiments of the  
14 invention, the oxygen scavenging material of either of the above methods  
15 comprises a polymeric backbone, cyclic olefinic pendent groups and linking  
16 groups linking the olefinic pendent groups to the polymeric backbone.

17 In a more preferred embodiment of the above-described embodiments of the  
18 invention, the polymeric backbone is ethylenic and the linking groups are  
19 selected from the group consisting of:

20  $-\text{O}-(\text{CHR})_n-$ ;  $-(\text{C}=\text{O})-\text{O}-(\text{CHR})_n-$ ;  $-\text{NH}-(\text{CHR})_n-$ ;  $-\text{O}-(\text{C}=\text{O})-(\text{CHR})_n-$ ;

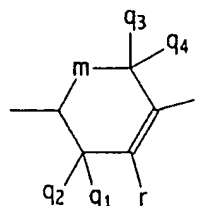
21  $-(\text{C}=\text{O})-\text{NH}-(\text{CHR})_n-$ ; and  $-(\text{C}=\text{O})-\text{O}-\text{CHOH}-\text{CH}_2-\text{O}-$ ;

22 wherein R is hydrogen or an alkyl group selected from the group consisting of  
23 methyl, ethyl, propyl and butyl groups and where n is an integer in the range  
24 from 1 to 12.

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1 In a more preferred embodiment of the above-described embodiments of the  
2 invention, the cyclic olefinic pendent groups have the structure (I):

3 (I)



4

5 where  $q_1$ ,  $q_2$ ,  $q_3$ ,  $q_4$ , and  $r$  are selected from the group consisting of  $-H$ ,  $-CH_3$ ,  
6 and  $-C_2H_5$ ; and where  $m$  is  $-(CH_2)_n-$  with  $n$  being an integer in the range from 0  
7 to 4; and wherein, when  $r$  is  $-H$ , at least one of  $q_1$ ,  $q_2$ ,  $q_3$  and  $q_4$  is  $-H$ .

8 In a more preferred embodiment of the above-described embodiments of the  
9 invention, the polymeric backbone comprises monomers selected from the  
10 group consisting of ethylene and styrene.

11 Other factors may also affect oxygen scavenging and should be considered  
12 when selecting compositions. These factors include but are not limited to  
13 temperature, relative humidity, and the atmospheric environment in the  
14 package.

15 The oxygen scavenging materials of the present invention are capable of  
16 altering the composition of the gases within the headspace of a package. The  
17 resulting advantage is an enhanced shelf life of food products. In one  
18 embodiment, the oxygen scavenger is incorporated as a layer in a polymer  
19 coated paperboard substrate material used to form a gable top carton for juice  
20 beverages.

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- 1 If the oxygen scavenger layer is used in such a polymer coated paperboard  
2 substrate material, formulation design may include, but not be limited to,  
3 coated substrate materials with the following structures:
- 4 (A) Polymer Coating Layer (LDPE/LLDPE)/Paperboard Substrate/Polymer  
5 Coating Layer/Barrier Layer (Metal Foil)/Tie Layer (Ethylene Acrylic Acid  
6 or Zinc Ionomer)/Oxygen Scavenging Layer/Polymer Coating Layer;
- 7 (B) Polymer Coating Layer/Paperboard Substrate/Polymer Coating  
8 Layer/Tie Layer/ Barrier Layer/Tie Layer/Oxygen Scavenging  
9 Layer/Polymer Coating Layer;
- 10 (C) Polymer Coating Layer/Paperboard Substrate/Polymer Coating  
11 Layer/Barrier Layer (Foil or Nylon)/Oxygen Scavenging Layer/Polymer  
12 Coating Layer;
- 13 (D) Polymer Coating Layer/Paperboard Substrate/Polymer Coating  
14 Layer/Tie Layer/Barrier Layer (EVOH or Nylon)/Tie Layer/Barrier  
15 Layer/Tie Layer/Oxygen Scavenging Layer/Polymer Coating Layer;
- 16 (E) Polymer Coating Layer/Paperboard Substrate/Barrier Layer  
17 (Nylon)/Barrier Layer (EVOH)/Tie Layer/Oxygen Scavenging  
18 Layer/Polymer Coating Layer;
- 19 (F) Polymer Coating Layer/Paperboard Substrate/Barrier Layer (Nylon)/Tie  
20 Layer/Oxygen Scavenging Layer/Polymer Coating Layer;
- 21 (G) Polymer Coating Layer/Paperboard Substrate/Polymer Coating  
22 Layer/Tie Layer/Barrier Layer (EVOH or Nylon)/Tie Layer/Oxygen  
23 Scavenging Layer/Polymer Coating Layer;

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- 1 (H) Polymer Coating Layer/Paperboard Substrate/Polymer Coating  
2 Layer/Tie Layer/Barrier Layer/Tie Layer/Oxygen Scavenging Layer/Tie  
3 Layer/Barrier Layer;
- 4 (I) Polymer Coating Layer/Paperboard Substrate/Polymer Coating  
5 Layer/Tie Layer/Barrier Layer/Tie Layer/Oxygen Scavenging Layer;
- 6 (J) Polymer Coating Layer/Paperboard Substrate/Polymer Coating  
7 Layer/Barrier Layer (Foil)/Tie Layer (Ethylene Acrylic Acid or Zinc  
8 Ionomer)/Oxygen Scavenging Layer;
- 9 (K) Polymer Coating Layer/Paperboard Substrate/Barrier Layer (Nylon)/Tie  
10 Layer/Oxygen Scavenging Layer; and
- 11 (L) Polymer Coating Layer/Paperboard Substrate/Polymer Coating  
12 Layer/Tie Layer/Barrier Layer (EVOH or Nylon)/Tie Layer/Oxygen  
13 Scavenging Layer/Polymer Coating Layer/Oxygen Scavenging  
14 Layer/Polymer Coating Layer.
- 15 The foregoing embodiments are particularly applicable to gable top or  
16 rectangular cartons, particularly when they contain a juice such as orange  
17 juice. It has been found that the most preferred oxygen scavenging material  
18 to use is a combination of a polymeric backbone, cyclic olefinic pendent  
19 groups and linking groups linking the olefinic pendent groups to the polymeric  
20 backbone.

21

### EXAMPLES

22 Experiments were performed with several kinds of orange juice containers to  
23 measure both the amount of oxygen in the headspace of the containers as  
24 well as the amount of oxygen dissolved in the juice and the amount of  
25 ascorbic acid contained in the juice over a period of six weeks.

### Example 1

A six-week shelf life study was conducted with orange juice packaged in commercial paperboard barrier laminate (PBL) cartons and in experimental carton samples using laminated board stock containing oxygen scavenging polymer in the inner layers of the cartons. PBL cartons consist of a laminated paperboard with a low density polyethylene coated on the outer surface of the paperboard and an oxygen barrier layer on the inside surface of the paperboard. The experimental oxygen scavenging (OS) cartons consisted of the PBL carton with a three-layer oxygen scavenging film (ABA Structure: Polyethylene/oxygen scavenging polymer/Polyethylene) further laminated on the inside surface of the oxygen barrier layer. PBL cartons containing loose strips of the three-layer oxygen scavenging film were also used. The oxygen scavenging films were one of three sizes: 4"x3½", 4"x7", and 4"x14".

The juice cartons were stored at 40°F and the orange juice was tested for ascorbic acid (vitamin C) and dissolved oxygen on a weekly basis. After six weeks, the orange juice packaged in the oxygen scavenger cartons retained a significantly greater amount of vitamin C as compared to the commercial PBL cartons.

Cartons were filled with orange juice and the amount of dissolved oxygen in the orange juice was measured using a YSI Dissolved Oxygen meter. The amount of vitamin C was measured by a visual titration method used extensively by the citrus industry, (AOAC Method, 1965, Official methods of Analysis, p. 764).

Orange juice in glass bottles was used as the control. PBL cartons were used as a standard. The oxygen scavenger laminate portion of the PBL carton with oxygen scavenger laminate was extrusion coated and later converted into trial cartons.

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1 The six packaging constructions filled with orange juice were:

2 (1) Glass — Control.

3 (2) PBL carton — Standard.

4 (3) PBL carton with oxygen scavenger laminate (OS).

5 (4) PBL carton with 4" x 3½" oxygen scavenger film strip (Film 3).

6 (5) PBL carton with 4" x 7" oxygen scavenger film strip (Film 4).

7 (6) PBL carton with 4" x 14" oxygen scavenger film strip (Film 5).

8 The oxygen scavenging cartons and films were exposed to ultra-violet light to  
9 activate the oxygen scavenger. The rapid decrease of dissolved oxygen in  
10 these cartons is noted in the data. The oxygen scavenger at day one,  
11 (week 0), had already begun to remove oxygen from the juice. By week one,  
12 the dissolved oxygen had dropped significantly and remained low throughout  
13 the study. This correlated with the retention of vitamin C in these cartons.

14 Agitation of the juice during filling increases the oxygen present in solution.  
15 The oxygen scavenger filmstrips, which were dropped into PBL cartons, were  
16 aggressive in removing oxygen from the orange juice but were not as effective  
17 as the extruded OS cartons. This may be due to the limited exposure and  
18 surface area of the strips in relation to the volume of the orange juice.

19 Graphs have been separated into four groups for ease of interpretation:

20 Figure 1) Vitamin C retention in glass container, PBL and OS cartons.

21 Figure 2) Amount of dissolved oxygen in glass, PBL and OS cartons.

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1 Figure 3) Vitamin C retention in OS carton and PBL cartons with OS  
2 film strips.

3 Figure 4) Dissolved oxygen in OS carton and PBL cartons with OS film  
4 strips.

5 **VITAMIN C DATA, MG/LITER**

WEEK	GLASS	PBL	OS	FILM 3	FILM 4	FILM 5
0	34.34	34.27	34.54	34.54	33.85	34.73
1	33.67	33.06	34.86	33.37	33.42	34.86
2	32.37	30.75	34.33	33.35	33.35	34.08
3	31.24	29.58	32.21	31.34	31.04	30.95
4	32.86	30.15	33.72	31.25	32.76	32.76
5	33.42	26.77	32.32	28.68	29.8	30.42
6	32.96	24.76	31.36	27.28	27.67	28.16

6

7 **TOTAL VITAMIN C LOSS AFTER SIX WEEKS**

	GLASS	PBL	OS	FILM 3	FILM 4	FILM 5
%	3.8	27.2	9.1	20.9	18.3	18.7

8

9 **DISSOLVED OXYGEN, MG/LITER**

WEEK	GLASS	PBL	OS	FILM 3	FILM 4	FILM 5
0.0	4.3	3.8	2.5	2.7	2.9	1.8
1.0	4.3	2.9	0.3	0.7	0.9	0.9
2.0	0.3	1.4	0.2	0.8	1.3	1.5

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3.0	0.1	1.0	0.3	1.1	1.1	0.9
4.0	0.2	1.0	0.8	0.8	1.1	1.1
5.0	0.2	1.6	1.0	0.4	1.5	1.3
6.0	0.2	<del>3.4</del>	<del>0.3</del>	<del>1.7</del>	2.3	4.0

1

2 Nutritional labeling of the orange juice requires that the stated percent of  
3 vitamin C be maintained through the out date posted on the carton. Oxygen  
4 will cause vitamin C to oxidize resulting in a loss of vitamin C. The purpose of  
5 the oxygen scavenger is to remove oxygen from the juice, from the package  
6 headspace, and any fugitive oxygen that permeates through the package wall.  
7 This action is accomplished by a catalyzed metal reaction of the scavenger  
8 polymer with oxygen. The oxygen scavenging polymer used in this test was a  
9 styrene/butadiene/styrene-based oxygen scavenger containing 1000 ppm of  
10 cobalt ion (as cobalt neodecanoate) and 1000 ppm of benzoylbiphenyl (BBP)  
11 photoinitiator.

12 Barrier films, such as polyamides used in PBL, slow the permeation rate of  
13 oxygen through the board structure, but do not remove the oxygen from the  
14 package headspace or contents. The oxygen scavenger works to remove  
15 residual and/or fugitive oxygen present in the package contents.

16 These preliminary results indicate that this oxygen scavenging package  
17 provides superior results for the extension of orange juice shelf life.



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1                                    Example 22                                    Organoleptic Tests

3    The organoleptics (negative effects on taste and odor) of the present  
4    invention were tested by comparing the taste of water and a fatty food  
5    packaged in an extrusion coated package having a layer of oxygen  
6    scavenging material incorporated as an internal layer of the package material  
7    with water and a fatty food packaged in a control package of identical  
8    structure but without the oxygen scavenging layer. Triangle tests with forced  
9    preferences were run using 28 trained panelists. In all cases, the sensory  
10   panel results showed a statistically significant ( $P < 0.0001$ ) preference for the  
11   packages containing the oxygen scavenging system over the control.

12   Although a few embodiments of the invention have been described in detail  
13   above, it will be appreciated by those skilled in the art that various  
14   modifications and alterations can be made to the particular embodiments  
15   shown without materially departing from the novel teachings and advantages  
16   of the invention. Accordingly, it is to be understood that all such modifications  
17   and alterations are included within the spirit and scope of the invention as  
18   defined by the following claims.

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## 1 WHAT IS CLAIMED IS:

- 2 1. A method of using oxygen scavenging material to decrease oxidation  
3 and maintain product properties in packaged beverages, foods, oxygen  
4 sensitive materials or oxygen sensitive components comprising the  
5 steps of:
- 6 (a) incorporating an oxygen scavenging material into the structure of a  
7 container used to package beverages, foods, oxygen sensitive  
8 materials or oxygen sensitive components;
- 9 (b) placing beverages, foods, oxygen sensitive materials or oxygen  
10 sensitive components in the container;
- 11 (c) sealing the container; and
- 12 (d) storing the container at a temperature between 20°F and 120°F;
- 13 wherein the oxygen scavenging material is selected from the group  
14 consisting of oxidizable polymers, ethylenically unsaturated polymers,  
15 benzylic polymers, allylic polymers, polybutadiene, poly[ethylene-methyl  
16 acrylate-cyclohexene acrylate] terpolymers, poly[ethylene-  
17 vinylicyclohexene] copolymers, polylimonene resins, poly  $\beta$ -pinene, poly  
18  $\alpha$ -pinene and a combination of a polymeric backbone, cyclic olefinic  
19 pendent groups and linking groups linking the olefinic pendent groups to  
20 the polymeric backbone.
- 21 2. The method of claim 1 wherein the method is performed under aseptic  
22 packaging conditions.
- 23 3. The method of claim 1 wherein the method is performed under cold-filled  
24 packaging conditions.

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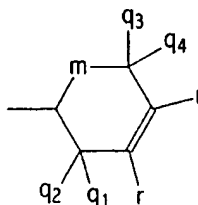
1 4. The method of claim 1, wherein the polymeric backbone of the  
 2 combination is ethylenic and the linking groups are selected from the  
 3 group consisting of:

4  $-O-(CHR)_n-$ ;  $-(C=O)-O-(CHR)_n-$ ;  $-NH-(CHR)_n-$ ;  $-O-(C=O)-(CHR)_n-$ ;

5  $-(C=O)-NH-(CHR)_n-$ ; and  $-(C=O)-O-CHOH-CH_2-O-$ ;

6 wherein R is hydrogen or an alkyl group selected from the group  
 7 consisting of methyl, ethyl, propyl and butyl groups and where n is an  
 8 integer in the range from 1 to 12.

9 5. The method of claim 1 wherein the cyclic olefinic pendent groups of the  
 10 combination have the structure (I):



11 (I)

12 where  $q_1$ ,  $q_2$ ,  $q_3$ ,  $q_4$ , and  $r$  are selected from the group consisting of  $-H$ ,  
 13  $-CH_3$ , and  $-C_2H_5$ ; and where  $m$  is  $-(CH_2)_n-$  with  $n$  being an integer in the  
 14 range from 0 to 4; and wherein, when  $r$  is  $-H$ , at least one of  $q_1$ ,  $q_2$ ,  $q_3$   
 15 and  $q_4$  is  $-H$ .

16 6. The method of claim 1 wherein the polymeric backbone of the  
 17 combination comprises monomers selected from the group consisting of  
 18 ethylene and styrene.

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- 1    7.    The method of claim 1 wherein the oxygen scavenging material is  
2        incorporated into the container as a film.
- 3    8.    The method of claim 7 wherein the film is a strip attached to the  
4        container's interior surface.
- 5    9.    The method of claim 7 wherein the film is a layer of the container's  
6        interior surface.
- 7    10.   The method of claim 9 wherein the container is manufactured from a  
8        paperboard comprising a laminated or coated oxygen barrier layer.
- 9    11.   The method of claim 1 wherein the container is a gable-top carton or a  
10       rectangular carton.
- 11   12.   The method of claim 1 wherein the container comprises an oxygen  
12       barrier.
- 13   13.   The method of claim 12 wherein the oxygen barrier comprises an  
14       oxygen scavenging composition.
- 15   14.   The method of claim 12 wherein the oxygen barriers are selected from  
16       the group consisting of polyamides, ethylene vinyl alcohol (EVOH),  
17       polyvinylidene chloride (PVDC), polyvinyl chloride (PVC), polyethylene  
18       terephthalate (PET), polyethylene naphthalate (PEN), polyacrylonitrile  
19       (PAN), and oxygen barrier films.
- 20   15.   The method of claim 14 wherein the oxygen barrier films are selected  
21       from the group consisting of polyamide films, ethylene vinyl alcohol films,  
22       silica coated films, foil, metallized films, nylon/EVOH/nylon, oriented  
23       polypropylene, polyester films, oriented polyethylene, and PVDC coated  
24       substrates.

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- 1 16. The method of claim 15 wherein the substrates of the PVDC coated  
2 substrates are selected from the group consisting of polypropylene,  
3 polyester, cellophane and paper.
- 4 17. The method of claim 15 wherein the substrates of the PVDC coated  
5 substrates are monolayer films or multi-layer films.
- 6 18. The method of claim 12 wherein the oxygen barriers are polymers, films  
7 or papers coated with silica oxide or metal oxide.
- 8 19. The method of claim 1 wherein the container comprises sealing layers.
- 9 20. The method of claim 1 wherein the material is an oxygen scavenging  
10 composition further comprising a transition metal catalyst.
- 11 21. The method of claim 20 wherein the oxygen scavenging composition is  
12 initiated by moisture or actinic radiation.
- 13 22. The method of claim 20 wherein the transition metal catalyst is a metal  
14 salt.
- 15 23. The method of claim 22 wherein the metal in the metal salt is cobalt.
- 16 24. The method of claim 22 wherein the metal salt is selected from the  
17 group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate,  
18 cobalt oleate and cobalt stearate.
- 19 25. The method of claim 20 wherein the oxygen scavenging composition  
20 further comprises at least one triggering material to enhance initiation of  
21 oxygen scavenging.
- 22 26. The method of claim 25 wherein the triggering material is a  
23 photoinitiator.

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- 1 27. The method of claim 1 wherein the oxygen scavenging material is  
2 initiated by moisture or actinic radiation.
- 3 28. A method of storing beverages, foods, oxygen-sensitive materials or  
4 oxygen-sensitive components for an extended period while maintaining  
5 product properties comprising the steps of:
- 6 (a) incorporating an oxygen scavenging material into the structure of a  
7 container used to package beverages, foods, oxygen-sensitive  
8 materials or oxygen-sensitive components;
- 9 (b) placing beverages, foods, oxygen sensitive materials or oxygen  
10 sensitive components in the container;
- 11 (c) sealing the container; and
- 12 (d) storing the container at a temperature between 20°F and 120°F;
- 13 wherein the oxygen scavenging material is selected from the group  
14 consisting of oxidizable polymers, ethylenically unsaturated polymers,  
15 benzylic polymers, allylic polymers, polybutadiene, poly[ethylene-methyl  
16 acrylate-cyclohexene acrylate] terpolymers, poly[ethylene-  
17 vinylcyclohexene] copolymers, polylimonene resins, poly  $\beta$ -pinene, poly  
18  $\alpha$ -pinene and a combination of a polymeric backbone, cyclic olefinic  
19 pendent groups and linking groups linking the olefinic pendent groups to  
20 the polymeric backbone.
- 21 29. The method of claim 28 wherein the method is performed under aseptic  
22 packaging conditions.
- 23 30. The method of claim 28 wherein the method is performed under  
24 cold-filled packaging conditions.

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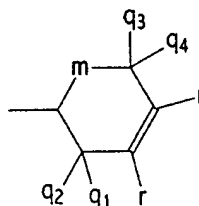
1 31. The method of claim 28 wherein the polymeric backbone of the  
 2 combination is ethylenic and the linking groups are selected from the  
 3 group consisting of:

4  $-O-(CHR)_n-$ ;  $-(C=O)-O-(CHR)_n-$ ;  $-NH-(CHR)_n-$ ;  $-O-(C=O)-(CHR)_n-$ ;

5  $-(C=O)-NH-(CHR)_n-$ ; and  $-(C=O)-O-CHOH-CH_2-O-$ ;

6 wherein R is hydrogen or an alkyl group selected from the group  
 7 consisting of methyl, ethyl, propyl and butyl groups and where n is an  
 8 integer in the range from 1 to 12.

9 32. The method of claim 28 wherein the cyclic olefinic pendent groups of the  
 10 combination have the structure (I):



11 (I)

12 where q<sub>1</sub>, q<sub>2</sub>, q<sub>3</sub>, q<sub>4</sub>, and r are selected from the group consisting of -H,  
 13 -CH<sub>3</sub>, and -C<sub>2</sub>H<sub>5</sub>; and where m is  $-(CH_2)_n-$  with n being an integer in the  
 14 range from 0 to 4; and wherein, when r is -H, at least one of q<sub>1</sub>, q<sub>2</sub>, q<sub>3</sub>  
 15 and q<sub>4</sub> is -H.

16 33. The method of claim 28 wherein the polymeric backbone comprises  
 17 monomers selected from the group consisting of ethylene and styrene.

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- 1    34. The method of claim 28 wherein the oxygen scavenging material is  
2        incorporated into the container as a film.
- 3    35. The method of claim 34 wherein the film is a strip attached to the  
4        container's interior surface.
- 5    36. The method of claim 34 wherein the film is a layer of the container's  
6        interior surface.
- 7    37. The method of claim 36 wherein the container is manufactured from a  
8        paperboard comprising a laminated or coated oxygen barrier layer.
- 9    38. The method of claim 28 wherein the container is a gable-top carton or a  
10       rectangular carton.
- 11   39. The method of claim 28 wherein the container comprises an oxygen  
12       barrier.
- 13   40. The method of claim 39 wherein the oxygen barrier comprises an  
14       oxygen scavenging composition.
- 15   41. The method of claim 39 wherein the oxygen barriers are selected from  
16       the group consisting of polyamides, ethylene vinyl alcohol (EVOH),  
17       polyvinylidene chloride (PVDC), polyvinyl chloride (PVC), polyethylene  
18       terephthalate (PET), polyethylene naphthalate (PEN), polyacrylonitrile  
19       (PAN), and oxygen barrier films.
- 20   42. The method of claim 41 wherein the oxygen barrier films are selected  
21       from the group consisting of polyamide films, ethylene vinyl alcohol films,  
22       silica coated films, foil, metallized films, nylon/EVOH/nylon, oriented  
23       polypropylene, polyester films, oriented polyethylene, and PVDC coated  
24       substrates.



- 1 43. The method of claim 42 wherein the substrates of the PVDC coated  
2 substrates are selected from the group consisting of polypropylene,  
3 polyester, cellophane and paper.
- 4 44. The method of claim 42 wherein the substrates of the PVDC coated  
5 substrates are monolayer films or multi-layer films.
- 6 45. The method of claim 41 wherein the oxygen barriers are polymers, films  
7 or papers coated with silica oxide or metal oxide.
- 8 46. The method of claim 28 wherein the container comprises sealing layers.
- 9 47. The method of claim 28 wherein the material is an oxygen scavenging  
10 composition further comprising a transition metal catalyst.
- 11 48. The method of claim 47 wherein the oxygen scavenging composition is  
12 initiated by moisture or actinic radiation.
- 13 49. The method of claim 47 wherein the transition metal catalyst is a metal  
14 salt.
- 15 50. The method of claim 49 wherein the metal in the metal salt is cobalt.
- 16 51. The method of claim 49 wherein the metal salt is selected from the  
17 group consisting of cobalt neodecanoate, cobalt 2-ethylhexanoate,  
18 cobalt oleate and cobalt stearate.
- 19 52. The method of claim 47 wherein the oxygen scavenging composition  
20 further comprises at least one triggering material to enhance initiation of  
21 oxygen scavenging.
- 22 53. The method of claim 52 wherein the triggering material is a  
23 photoinitiator.

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- 1 54. The method of claim 28 wherein the oxygen scavenging material is  
2 initiated by moisture or actinic radiation.
- 3 55. A rigid paperboard container, the container being constructed from  
4 extrusion coated or laminated paperboard comprising:
- 5 (a) a paperboard substrate having opposed inner and outer surfaces;
- 6 (b) a first polymer layer coated or laminated onto the outer surface of  
7 said paperboard substrate; and
- 8 (c) an inner product contact sandwich layer comprising an oxygen  
9 barrier layer and an oxygen scavenging layer;
- 10 wherein the oxygen scavenging material is selected from the group  
11 consisting of oxidizable polymers, ethylenically unsaturated polymers,  
12 benzylic polymers, allylic polymers, polybutadiene, poly[ethylene-methyl  
13 acrylate-cyclohexene acrylate] terpolymers, poly[ethylene-  
14 vinylcyclohexene] copolymers, polylimonene resins, poly  $\beta$ -pinene, poly  
15  $\alpha$ -pinene and a combination of a polymeric backbone, cyclic olefinic  
16 pendent groups and linking groups linking the olefinic pendent groups to  
17 the polymeric backbone.
- 18 56. A rigid paperboard container according to claim 55 wherein the inner  
19 product contact sandwich layer further comprises a tie layer adjacent to  
20 the barrier layer.
- 21 57. A rigid paperboard container according to claim 55 wherein the inner  
22 product contact sandwich layer further comprises a seal layer coating or  
23 laminating the innermost surface of the inner product contact sandwich  
24 layer.

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- 1 58. A rigid paperboard container according to claim 55 wherein a second  
2 polymer layer is coated or laminated onto the inner surface of said  
3 paperboard substrate.
- 4 59. A rigid paperboard container according to claim 58 wherein a tie layer is  
5 juxtaposed between the barrier layer and the second polymer layer  
6 coated or laminated onto the inner surface of the paperboard substrate.
- 7 60. A rigid paperboard container according to claim 55 wherein a third  
8 polymer layer is coated or laminated onto the inner surface of the  
9 oxygen scavenging layer of the inner product contact sandwich layer.
- 10 61. A rigid paperboard container according to claim 60 wherein the inner  
11 product contact sandwich layer further comprises a fourth polymer layer  
12 and a second oxygen scavenging layer, the second oxygen scavenging  
13 layer being on the inner surface of the third polymer layer and the fourth  
14 polymer layer coating or laminating the inner surface of the second  
15 oxygen scavenging layer.
- 16 62. A rigid paperboard container according to claim 60 wherein a tie layer is  
17 coated or laminated onto the inner surface of the oxygen scavenging  
18 layer and an ethylene vinyl alcohol layer is coated or laminated onto the  
19 inner surface of the tie layer coating or laminating the inner surface of  
20 the oxygen scavenging layer.
- 21 63. A rigid paperboard container according to claim 60 wherein the inner  
22 product contact sandwich layer further comprises a second barrier layer  
23 and a second tie layer, the second barrier layer being on the inner  
24 surface of the first tie layer and the second tie layer being juxtaposed  
25 between the inner surface of the second barrier layer and the outer  
26 surface of the oxygen scavenging layer.

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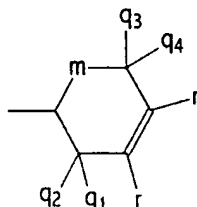
1 64. A rigid paperboard container according to claim 55 wherein the  
 2 polymeric backbone of the combination is ethylenic and the linking  
 3 groups are selected from the group consisting of:

4  $-O-(CHR)_n-$ ;  $-(C=O)-O-(CHR)_n-$ ;  $-NH-(CHR)_n-$ ;  $-O-(C=O)-(CHR)_n-$ ;

5  $-(C=O)-NH-(-CHR)_n-$ ; and  $-(C=O)-O-CHOH-CH_2-O-$ ;

6 wherein R is hydrogen or an alkyl group selected from the group  
 7 consisting of methyl, ethyl, propyl and butyl groups and where n is an  
 8 integer in the range from 1 to 12.

9 65. A rigid paperboard container according to claim 55 wherein the cyclic  
 10 olefinic pendent groups of the combination have the structure (I):



11 (I)

12 where  $q_1$ ,  $q_2$ ,  $q_3$ ,  $q_4$ , and  $r$  are selected from the group consisting of  $-H$ ,  
 13  $-CH_3$ , and  $-C_2H_5$ ; and where  $m$  is  $-(CH_2)_n-$  with  $n$  being an integer in the  
 14 range from 0 to 4; and wherein, when  $r$  is  $-H$ , at least one of  $q_1$ ,  $q_2$ ,  $q_3$   
 15 and  $q_4$  is  $-H$ .

16 66. A rigid paperboard container according to claim 55 wherein the  
 17 polymeric backbone of the combination comprises monomers selected  
 18 from the group consisting of ethylene and styrene.

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- 1 67. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
2 61, 62 or 63 wherein the polymer layer or the seal layer is selected from  
3 the group consisting of low density polyethylene polymer, linear low  
4 density polyethylene polymer, a blend of low density polyethylene  
5 polymer and linear low density polyethylene polymer, and a coextrusion  
6 of low density polyethylene polymer and linear low density polyethylene  
7 polymer.
- 8 68. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
9 61, 62 or 63 wherein the tie layer of the inner product contact sandwich  
10 layer comprises ethylene acrylic acid.
- 11 69. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
12 61, 62 or 63 wherein the tie layer of the inner product contact sandwich  
13 layer comprises ethylene methacrylic acid.
- 14 70. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
15 61, 62 or 63 wherein the tie layer of the inner product contact sandwich  
16 layer comprises maleated tie layer polymers.
- 17 71. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
18 61, 62 or 63 wherein the tie layer of the inner product contact sandwich  
19 layer comprises ionomer.
- 20 72. A rigid paperboard container according to claim 71 wherein the tie layer  
21 of the inner product contact sandwich layer comprises zinc ionomer.
- 22 73. A rigid paperboard container according to claim 71 wherein the tie layer  
23 of the inner product contact sandwich layer comprises sodium ionomer.

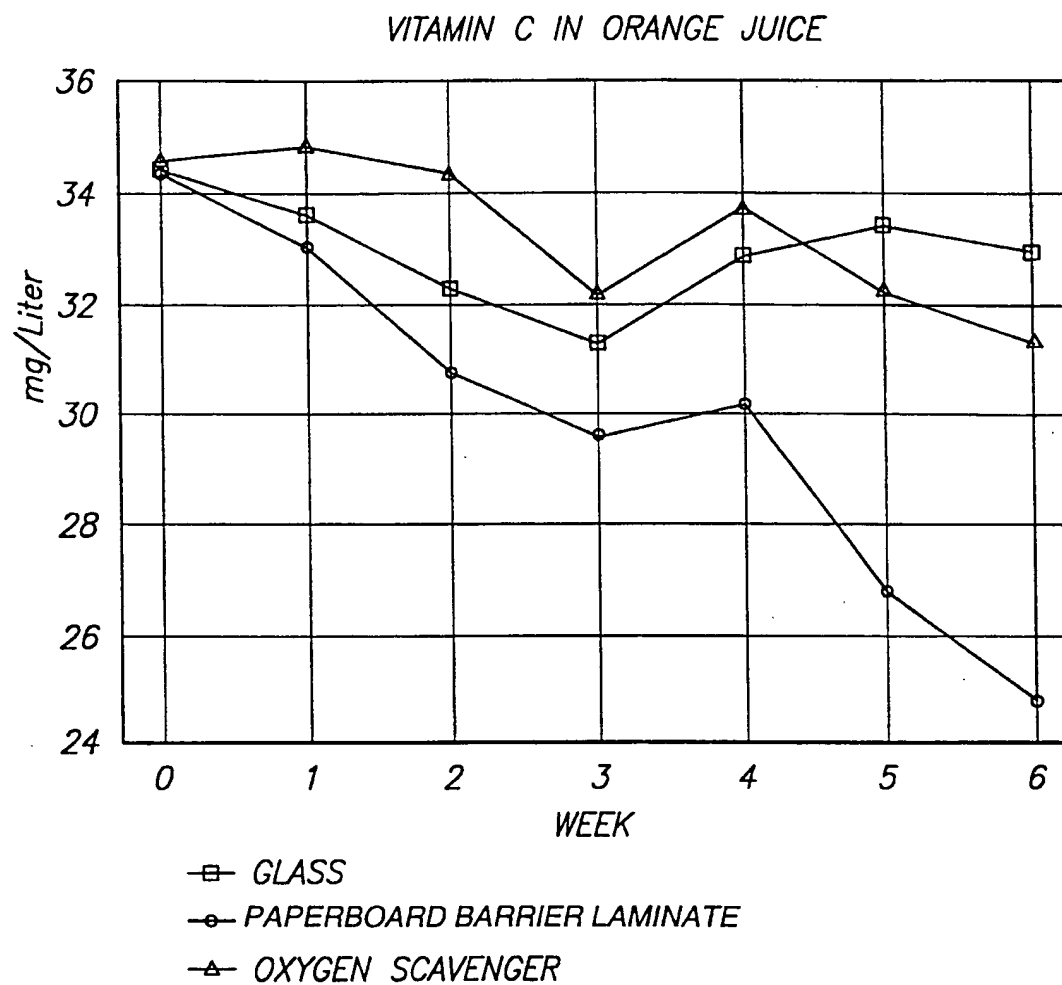
-44-

- 1 74. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
2 61, 62 or 63 wherein the barrier layer of the inner product contact  
3 sandwich layer comprises foil.
- 4 75. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
5 61, 62 or 63 wherein the barrier layer of the inner product contact  
6 sandwich layer comprises metallized film.
- 7 76. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
8 61, 62 or 63 wherein the barrier layer of the inner product contact  
9 sandwich layer comprises ethylene vinyl alcohol (EVOH).
- 10 77. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
11 61, 62 or 63 wherein the barrier layer of the inner product contact  
12 sandwich layer comprises polyamides.
- 13 78. A rigid paperboard container according to claim 77 wherein an ethylene  
14 vinyl alcohol (EVOH) layer is coated onto at least one of the inner and  
15 outer surfaces of the polyamides barrier layer.
- 16 79. A rigid paperboard container according to claim 55, 56, 57, 58, 59, 60,  
17 61, 62 or 63 wherein an ethylene vinyl alcohol (EVOH) layer is coated  
18 onto at least one of the inner and outer surfaces of the barrier layer.
- 19 80. The paperboard container according to claim 55, 56, 57, 58, 59, 60, 61,  
20 62 or 63 wherein the container is a gable top carton or a rectangular  
21 carton.
- 22 81. The paperboard container according to claim 80 wherein the container  
23 contains juice.
- 24 82. The paperboard container according to claim 81 wherein the container  
25 contains orange juice.

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- 1 83. The paperboard container according to claim 80 wherein the oxygen
  - 2 scavenging material is a combination of a polymeric backbone, cyclic
  - 3 olefinic pendent groups and linking groups linking the olefinic pendent
  - 4 groups to the polymeric backbone.
- ~~\_\_\_\_\_~~

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**FIG. 1**



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## OXYGEN IN ORANGE JUICE

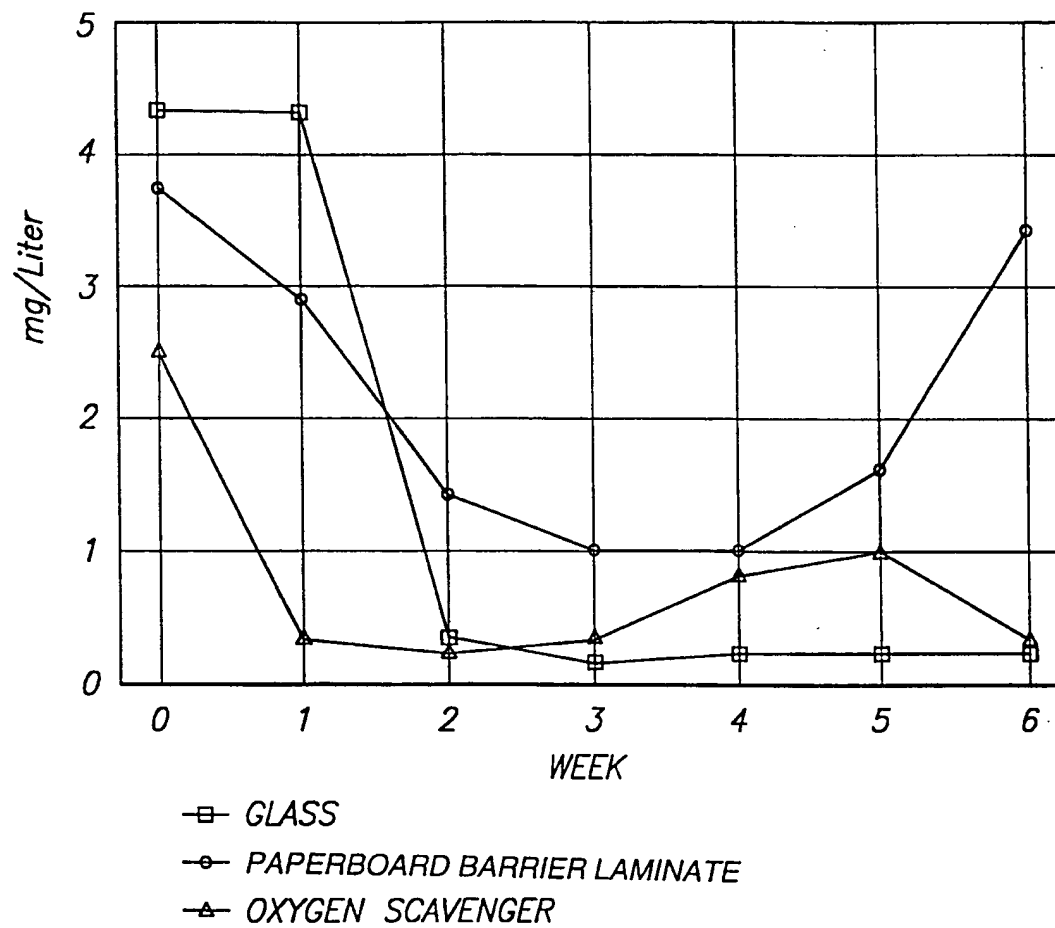


FIG. 2

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## VITAMIN C RETENTION WITH OXYGEN SCAVENGER

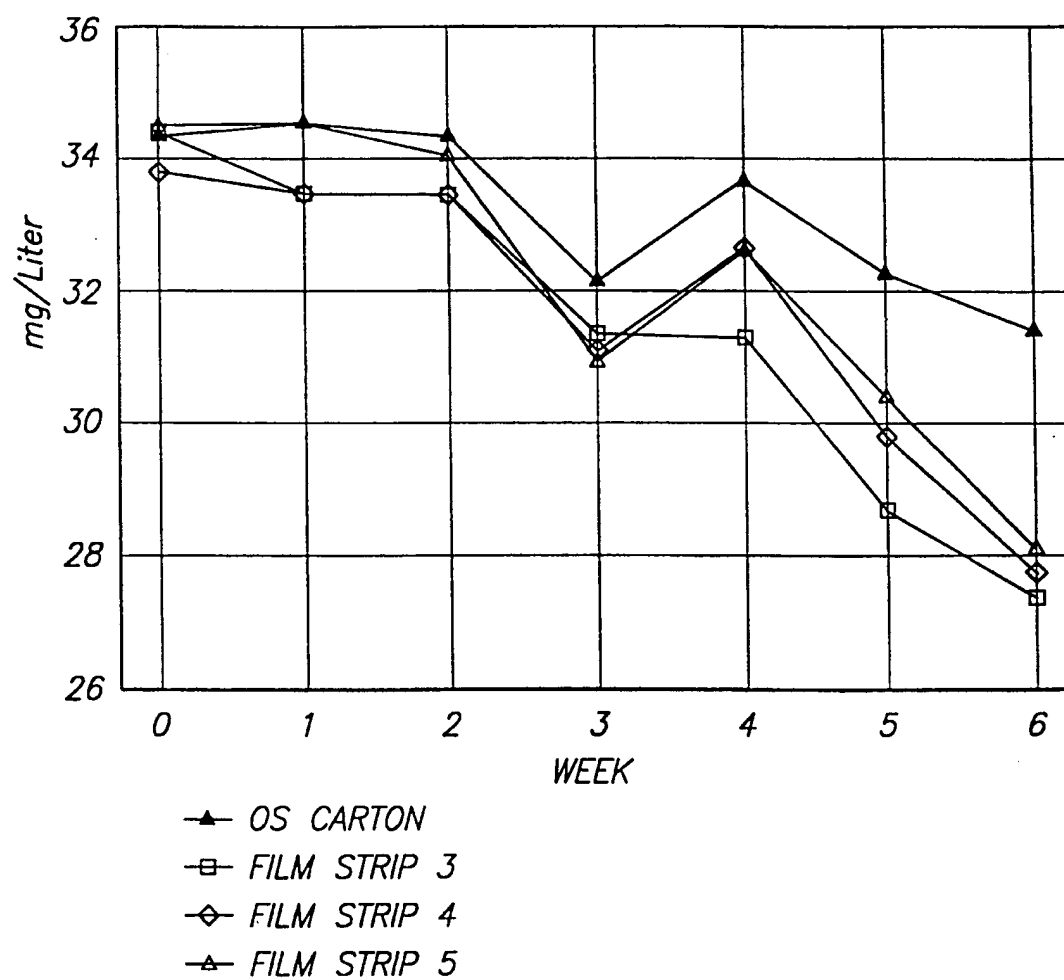


FIG. 3

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## OXYGEN IN ORANGE JUICE

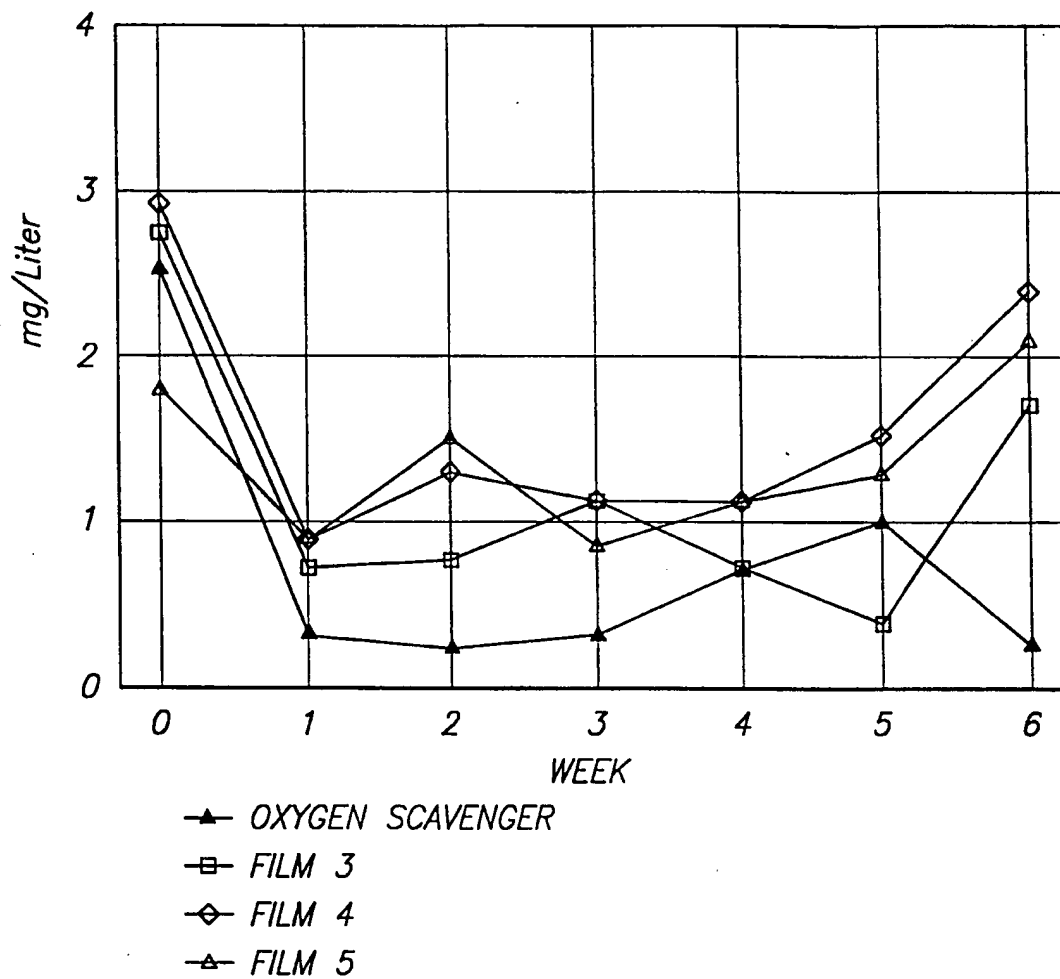


FIG. 4

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/18781

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A23L3/3436

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 507 207 A (GRACE W R & CO) 7 October 1992 (1992-10-07)	1-83
Y	page 3, line 15 - line 17 ---	1-83
X	WO 98 06779 A (CHEVRON CHEM CO) 19 February 1998 (1998-02-19)	1-83
Y	page 4, line 5 - line 14 ---	1-83
X	GB 2 036 012 A (OREAL) 25 June 1980 (1980-06-25)	1-83
	page 1, right-hand column, line 85 - line 104 ---	
X	WO 96 40799 A (CHEVRON CHEM CO) 19 December 1996 (1996-12-19)	1-83
	page 30, line 13 -page 32, line 13 page 47, line 21 -page 48, line 19 ---	
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

24 November 1999

Date of mailing of the international search report

13/12/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Bendl, E

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/18781

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 794 053 A (GRACE W R & CO) 10 September 1997 (1997-09-10) page 3, line 2 - line 58 -----	1-83
X	WO 94 07379 A (GRACE W R & CO) 14 April 1994 (1994-04-14)	1-83
Y	page 4, line 22 -page 5, line 32 -----	1-83
X	WO 94 07944 A (GRACE W R & CO) 14 April 1994 (1994-04-14) page 7, line 6 - line 30 -----	1-83

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 99/18781

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0507207 A	07-10-1992	AU 657728 B	23-03-1995
		AU 1141092 A	08-10-1992
		CA 2062083 A	03-10-1992
		CS 9201000 A	14-10-1992
		FI 921425 A	03-10-1992
		HU 67219 A	28-03-1995
		IL 101161 A	14-05-1996
		JP 5115776 A	14-05-1993
		MX 9201379 A	01-10-1992
		NO 921268 A	05-10-1992
		NZ 241802 A	22-12-1994
		PL 171849 B	30-06-1997
		PL 172483 B	30-09-1997
		RU 2092513 C	10-10-1997
		US 5346644 A	13-09-1994
		US 5529833 A	25-06-1996
		US 5700554 A	23-12-1997
		US 5350622 A	27-09-1994
		ZA 9201914 A	16-09-1993
WO 9806779 A	19-02-1998	US 5776361 A	07-07-1998
		AU 3963597 A	06-03-1998
		EP 0918818 A	02-06-1999
		NO 990674 A	19-03-1999
GB 2036012 A	25-06-1980	FR 2439769 A	23-05-1980
		DE 2943166 A	08-05-1980
		US 4281192 A	28-07-1981
		US 4339561 A	13-07-1982
WO 9640799 A	19-12-1996	AU 5632696 A	30-12-1996
		BR 9609232 A	11-05-1999
		CA 2218381 A	19-12-1996
		EP 0830386 A	25-03-1998
		JP 11506150 T	02-06-1999
EP 0794053 A	10-09-1997	US 5942297 A	24-08-1999
WO 9407379 A	14-04-1994	US 5310497 A	10-05-1994
		AT 162689 T	15-02-1998
		AU 677240 B	17-04-1997
		AU 5140293 A	26-04-1994
		BR 9307155 A	30-03-1999
		CA 2146026 A	14-04-1994
		DE 69316765 D	05-03-1998
		DE 69316765 T	10-06-1998
		DK 663800 T	30-03-1998
		EP 0663800 A	26-07-1995
		ES 2113554 T	01-05-1998
		FI 951537 A	23-05-1995
		IL 107137 A	13-07-1997
		JP 8502202 T	12-03-1996
		MX 9306020 A	29-07-1994
		NZ 256613 A	20-12-1996
		US 5648020 A	15-07-1997
		ZA 9307137 A	27-03-1995
WO 9407944 A	14-04-1994	US 5399289 A	21-03-1995

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 99/18781

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9407944 A		AT 176263 T	15-02-1999
		AU 673011 B	24-10-1996
		AU 5140393 A	26-04-1994
		BR 9307156 A	30-03-1999
		DE 69323319 D	11-03-1999
		DE 69323319 T	02-06-1999
		EP 0662986 A	19-07-1995
		EP 0854166 A	22-07-1998
		ES 2128439 T	16-05-1999
		FI 951538 A	23-05-1995
		GR 3029971 T	30-07-1999
		IL 107136 A	13-07-1997
		JP 8502306 T	12-03-1996
		NZ 256614 A	20-12-1996